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<p>(54) Title: REDUCED SOLVENT ANTISTATIC HARD COAT</p> <p>(57) Abstract</p> <p>A cured antistatic coating comprising a fluorinated ionic salt of general formula (1), wherein M⁺ represents a cation, Q represents a carbon atom, a nitrogen atom, or an oxygen atom, each X independently represents a divalent linking group, R_f represents a fluorinated group; and R' represents a monovalent organic group. When Q is carbon c is 3 and m is 1, 2, or 3; when Q is nitrogen c is 2 and m is 1 or 2, and when Q is oxygen, c is 1 and m is 1. In another embodiment, the above fluorinated ionic salt may be incorporated into an antistatic coating obtained from ingredients comprising a radiation-curable material; a nonionic perfluoro surfactant; and a radiation-curable silicone-containing compound.</p> <div style="text-align: center;"> $\begin{array}{c} \text{M}^+\text{Q} \begin{cases} \text{[XR}_f\text{]}_m \\ \text{[XR']}_{c-m} \end{cases} \end{array} \quad (1)$ </div>		

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REDUCED SOLVENT ANTISTATIC HARD COAT**FIELD OF THE INVENTION**

The present invention relates generally to the use of antistatic hard coat compositions, such as for use on optical media, and more specifically to antistatic hard coat compositions comprising a fluorinated ionic salt.

BACKGROUND OF THE INVENTION

Optical recording media typically comprise an optical recording layer provided on a substrate. For media such as magneto optic recording media and WORM (write-once-read-many) optical recording media, the optical recording layer generally contains a thin film rare earth transition metal alloy such as gadolinium-cobalt (Gd-Co), gadolinium-iron (Gd-Fe), terbium-iron (Tb-Fe), dysprosium-iron (Dy-Fe), Gd-Tb-Fe, Tb-Dy-Fe, Tb-Fe-Co, terbium-iron-chromium (Tb-Fe-Cr), gadolinium-iron-bismuth (Gd-Fe-Bi), Gd-Co-Bi, gadolinium-iron-tin (Gd-Fe-Sn), Gd-Fe-Co, Gd-Co-Bi, or Gd-Dy-Fe. Such alloys are described, for example, in U.S. Pat. No. 4,822,675. For media such as compact disks, the optical recording layer may be a layer of reflective material, for example an aluminum or aluminum alloy, having a patterned, information-bearing surface.

Many of the materials which are suitable for the optical recording layer of optical disks react strongly with oxygen and other elements which may be present in the environment in which optical recording media are used. Furthermore, the substrate itself may contain impurities which react with the optical recording layer. Thus, transparent dielectric films may be deposited on one or both sides of the optical recording layer to protect it. Such dielectric films are described, for example, in U.S. Pat. Nos. 4,833,043 and 4,917,970.

Optionally a reflective layer may be incorporated into optical recording media so that incident light that passes through the optical recording layer a first time is reflected and passes back through the optical recording layer a second time. Such reflection increases the magneto optic rotation of incident light because the so-called Faraday effect is added to the so-called Kerr effect.

The reflective layer may be incorporated into a magnetic recording medium such that the optical recording layer is interposed between the substrate and the reflective layer. For such media, transparent substrates are used so that incident light passes first through the substrate, then passes through the optical recording layer, and then is reflected by the reflective layer back through the optical recording layer. Such media are known as substrate incident media. Alternatively, when the optional reflective layer is disposed between the substrate and the optical recording layer, the read and write beams will not be directed through the substrate. Such a medium is known as an air incident medium, although generally there is at least one layer between the optical recording layer and the air.

For substrate incident media, the substrate is typically formed from polycarbonate. Polycarbonate substrates have excellent rigidity, dimensional stability, transparency, and impact strength, but unfortunately have poor abrasion resistance. Consequently, polycarbonate substrates are susceptible to physical damage from scratches, abrading, and the like.

To protect the substrate from physical damage, a "hard coat" layer is coated onto the substrate to form a protective barrier between the substrate and the air. For example, Japanese Kokai No. JP02-260145 describes a hard coat layer that is coated onto the substrate of an optical card. The hard coat layer is formed from an electron-beam or ultraviolet radiation-curable resin.

The hard coat layers may incorporate useful ingredients into the composition. For example, the hard coat layer of Japanese Kokai No. JP02-260145 also includes a surface slipping agent, i.e., a lubricant.

Another example is the use of antistatic agents incorporated into the hard coat composition. Static charge build-up attracts dust to the hard coat layer of optical recording media. Dust can prevent read and write beams from reaching the optical recording layer during writing or reading and thereby cause data errors which reduce the usefulness of the optical recording media. Thus, it is generally desirable to incorporate antistatic agents such as ionic salts into the hard coat layer in order to reduce this static charge build-up and prevent the attendant dust attraction and data errors from occurring.

Antistatic hard coat compositions must satisfy stringent requirements in order to be suitable for use in optical recording media. In addition to providing protection

against the build-up of static charge, cured antistatic hard coat layers must be transparent, abrasion resistant, and compositionally stable so that the compositions remain transparent for long periods of time. If the compositions become hazy, the amount of incident light that reaches the optical recording layer may be reduced, thus
5 causing an increase in bit error rate or error in the read/write cycles.

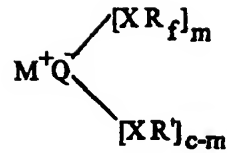
Another requirement of antistatic hard coat compositions concerns the viscosity of the uncured antistatic composition. Typically, the cured antistatic hard coat is produced from an uncured admixture of ingredients which are first coated onto the optical recording media substrate, then cured. One method of applying antistatic hard
10 coats to polycarbonate substrates is by a spin coating technique. The spin coating technique requires that the viscosity of the uncured antistatic hard coat admixture be relatively low. For instance, to obtain an antistatic hard coat layer of uniform thickness by the spin coating technique, the antistatic composition preferably must have low viscosity, e.g., 100 centipoise or less at 25 C. The ingredients of conventional hard
15 coat compositions, however, may exhibit a relatively higher molecular weight and surface tension. This combination of properties causes admixtures of conventional hard coat compositions to be too viscous to spin coat. One method by which the viscosity of these admixtures can be reduced is by adding a solvent to the admixture. Solvents are generally disfavored because of their negative health and environmental effects.

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SUMMARY OF THE INVENTION

The present inventors have found that certain fluorinated ionic salts very effectively dissipate static charge when included in a layer coated onto a substrate. These fluorinated ionic salts have proven to be especially effective when used with
25 certain classes of nonionic surfactants. The present inventors have further discovered that these fluorinated ionic salts can be incorporated into hard coat formulations that have superior antistatic and physical properties, and that can be coated without needing to be further diluted with solvents.

An aspect of the present invention is an optical recording disk having a hard
30 coat layer provided on at least one surface of the disk, wherein the hard coat layer comprises a fluorinated ionic salt of the general formula:



wherein M^+ represents a cation, Q represents a carbon atom, a nitrogen atom, or an oxygen atom; each X independently represents a divalent linking group, R_f represents a fluorinated group; R' represents a monovalent organic group; and when Q is carbon, c is 3 and m is 1 or 2 or 3, when Q is nitrogen, c is 2 and m is 1 or 2; and when Q is oxygen, c is 1 and m is 1.

A further aspect of the present invention is an optical recording disk having a hard coat layer provided on at least one surface of the disk, wherein the hard coat layer is a cured composition obtained from ingredients comprising a fluorinated ionic salt; a radiation-curable component; a nonionic fluorinated surfactant; and a radiation-curable silicone-containing compound. Preferably, the radiation-curable component comprises a (meth)acrylate-functional diluent; a multi-functional (meth)acrylate monomer comprising three or more (meth)acrylate groups; and a multi-functional (meth)acrylate oligomer.

Yet a further aspect of the present invention is a cured antistatic coating obtained from ingredients comprising a fluorinated ionic salt; a radiation-curable component; a nonionic surfactant; and a radiation-curable silicone-containing compound. Preferably, the radiation-curable component comprises a (meth)acrylate-functional diluent; a multi-functional (meth)acrylate monomer comprising three or more (meth)acrylate groups; and a multi-functional (meth)acrylate oligomer.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a schematic cross-section of a magneto optic recording medium comprising an antistatic hard coat of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

Figure 1 shows a greatly enlarged schematic cross-section through a portion of an illustrative substrate incident magneto optic ("MO") recording disk of the present invention. It is to be understood, however, that the antistatic compositions of the

present invention are not limited solely to use on MO media, but rather are suitable for use on a wide variety of materials. For example, in addition to being used with MO disks, the antistatic compositions of the present invention are particularly suitable for use with other kinds of optical recording media such as compact disks, CD-ROM, CD-R, WORM (i.e., write-once-read-many) media, and the like. Further, the invention may be useful in many other coating applications, including those where the dissipation of static charge is important.

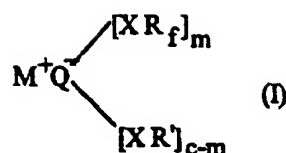
Referring now to figure 1, an optical recording layer 12 is provided on a transparent substrate 14. A film 16 having a reflective surface 18 is disposed to reflect incident light 40 which will have been transmitted through the optical recording layer 12 a first time back through the optical recording layer 12 a second time. A protective sealcoat 20 is disposed over the film 16 to protect the film 16 and reflective surface 18 from the environment. Optionally, transparent dielectric layers 15 and 17 may be disposed on one or both sides of the optical recording layer 12. As is known in the art, such dielectric layers enhance the optical signal from the optical recording layer 12 and also protect the optical recording layer 12 from oxidation or corrosion due to heat, humidity, or chemical reactions with impurities, such as moisture. A hard coat layer 22 of the present invention is provided over the substrate 14 to protect the substrate 14 from physical damage.

The substrate 14, optical recording layer 12, film 16, protective sealcoat 20, and the dielectric layers 15 and 17 can be of a type known in the art. However, the substrate 14 is preferably formed from polycarbonate because the antistatic compositions of the present invention show excellent adhesion to polycarbonate substrates.

The cured hard coat layer 22 is a cured composition obtained from ingredients comprising a fluorinated ionic salt, a radiation-curable component, a nonionic fluorinated surfactant, and a radiation-curable silicone-containing compound.

In the practice of the present invention, useful fluorinated ionic salts improve the conductivity of a cured antistatic hard coat thereby preventing the accumulation of static charge buildup. A wide variety of fluorinated ionic salts could be used. U.S. Pat. No. 5,176,943 (Woo), at column 6 (incorporated herein by reference), describes some examples of the fluorinated ionic salts that can be used in this invention.

One class of preferred fluorinated ionic salt is the class generally described by formula I



wherein M^+ represents a cation such as, for example, Na^+ , Li^+ , K^+ , H^+ , $\text{R}_x\text{NH}_{4-x}^+$, Ca^{2+} , Zn^{2+} , etc., preferably Li^+ ; Q represents either a carbon atom, a nitrogen atom,
 5 or an oxygen atom; each X independently represents divalent linking groups, preferably a sulfonyl group ($-\text{SO}_2-$) or a carbonyl group ($-\text{C}(\text{O})-$); c represents an integer equal to one less than the valency of the Q atom; and m is from 1 to c. Specifically, when Q is an oxygen atom having a valency 2, c is 1 and m is 1. When Q is a nitrogen atom having a valency 3, c is 2 and m is 1 or 2. When Q is a carbon atom having a valency
 10 4, c is 3 and m is 1, 2, or 3.

In formula I, R' is generally a monovalent organic group, preferably an alkyl or aryl moiety. Examples of preferred R' groups include but are not limited to halogen-substituted alkyl and aryl groups. Where R' contains more than one carbon atom in a skeletal chain, the skeletal chain may contain heteroatoms such as N, O, and S
 15 interrupting the skeletal carbon chain. Where m is equal to c a fluorinated ionic salt will have no $\text{X-R}'$ group. Also, the R' and R_f groups may be linked to form a cyclic molecule.

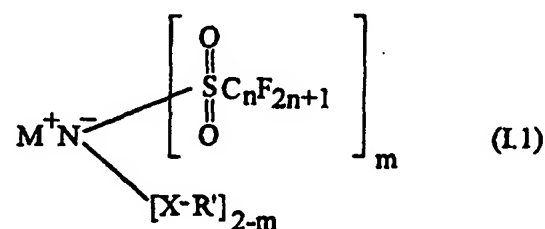
R_f in formula I is a monovalent, fluorinated, moiety that contains at least one carbon atom. Where R_f contains more than one carbon atom in a skeletal chain, the
 20 chain may be branched or cyclic, but is preferably straight and may be saturated or unsaturated. The chain of carbon atoms may be interrupted by heteroatoms or radicals, such as oxygen, sulfur, or nitrogen atoms. Preferably, where such heteroatoms are present, the skeletal chain does not contain more than one heteroatom for every two carbon atoms. An occasional carbon-bonded hydrogen atom, bromine atom, or chlorine
 25 atom may be present; where present, however, these atoms preferably are present not more than once for every two carbon atoms. R_f is preferably perfluorinated.

The total number of carbon atoms in R_f can vary and can be, for example, from 1 to 18, and is preferably from 1 to 8. Where R_f is or contains a cyclic structure, such structure preferably has 5 or 6 ring members, one or two of which can be
 30 heteroatoms, e.g., oxygen and/or nitrogen. The R_f group is also preferably saturated,

e.g., free of ethylenic or other carbon-to-carbon unsaturation. Examples of R_f groups are fluorinated alkyl, e.g., CF_3 -, and alkyloxyalkyl, e.g., CF_3OCF_2 -, preferred R_f moieties are perfluorinated, straight chain aliphatic moieties containing only carbon and fluorine atoms and having from 1 to 8 carbon atoms. In those instances wherein the
 5 fluorinated ionic salt of formula I contains more than one R_f moiety, such R_f moieties can be the same or different, and optionally can be linked to form a cyclic molecule.

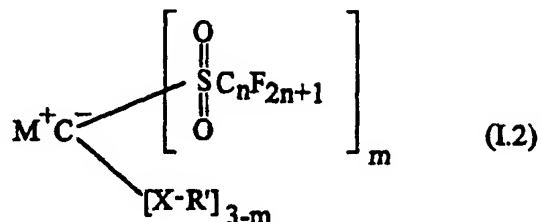
While not wishing to be bound by theory, fluorinated ionic salts described by formula I are believed to be effective within antistatic hard coat compositions because these salts are believed to form complexes with the polyoxyethylene segments of the
 10 nonionic fluorinated surfactants preferred in the practice of the present invention. It is further postulated that in order to minimize interfacial tension, the fluorinated segment of the nonionic fluorinated surfactant migrates to and orients itself at the coating surface or air interface, causing the entire nonionic fluorinated surfactant/fluorinated ionic salt
 15 coating surface by the fluorinated ionic salt. By being concentrated at the surface of the antistatic hard coat layer, the conductive fluorinated ionic salt acts very effectively as an antistatic agent to dissipate electrostatic charge.

Preferred fluorinated ionic salts according to formula I include, e.g., (perfluoroalkyl sulfonyl) imide salts, (perfluoroalkyl sulfonyl) methide salts, and
 20 perfluoroalkylsulfonate salts. Perfluoroalkyl sulfonyl imide salts can be described by the general formula



where m is 1 or 2, preferably 2, n is in the range from about 1 to 12, preferably from about 1 to 8, M, and R' are as defined above; X is preferably $-SO_2-$ or
 25 $-C(O)-$, most preferably $-SO_2-$.

Perfluoroalkyl sulfonyl methide salts are described by the general formula



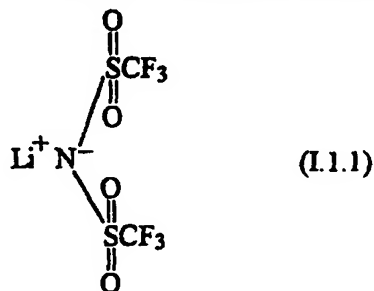
where m is 1 or 2 or 3, preferably 3, n is in the range from about 1 to 12, preferably from about 1 to 8, M, and R' are as defined above; X is preferably -SO₂- or
 5 -C(O)-, most preferably -SO₂-.

Perfluoroalkylsulfonate salts can be described by the general formula



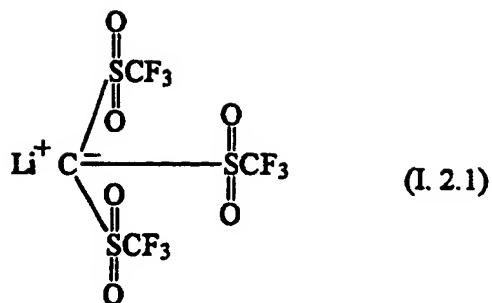
10 M is as defined above. Preferably R_f has the general formula C_nF_{2n+1}, wherein n is preferably in the range from 1 to 8, most preferably 1 to 4.

A specific example of formula I.1 is bis-perfluoroalkylsulfonyl imide salts; especially preferred is lithium bis-(trifluoromethylsulfonyl)imide:



15 available from 3M Corp. under the trade name Fluorad HQ-115. Processes generally useful for the synthesis of fluorochemical imide salts and their conjugate acids are described in the following references: U.S. Pat. No. 4,505,997 (Armand et al.); U.S. Pat. No. 5,072,040 (Armand); Darryl D. DesMarteau, Chemistry of
 Perfluoromethylsulfonyl Perfluorobutylsulfonyl Imide, *Inorg. Chem.* **29**, 2982-85
 20 (1990); and Darryl D. DesMarteau, Synthesis, Properties, and Reactions of
 Bis((trifluoromethyl)sulfonyl) Imide, *Inorg. Chem.* **23**, 372-23 (1984).

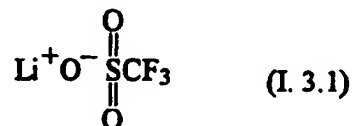
A specific example of formula I.2 is tris-(perfluoroalkylsulfonyl) methide salts; especially preferred is lithium tris-(trifluoromethylsulfonyl) methide:



Processes useful for the synthesis of fluorochemical methide salts and their conjugate acids are described in U.S. Pat. No. 5,273,840 (Dominey) and in Turowsky & Seppelt, *Inorg. Chem.*, 27, 2135-37 (1988).

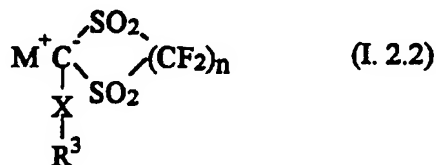
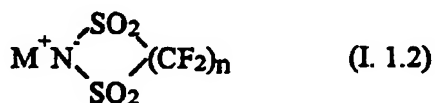
A specific example of formula I.3 is lithium trifluoromethanesulfonate:

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commercially available from 3M Corp. under the trade name Fluorad FC-122.

Cyclic analogs of the salts according to formulas I.1 and I.2 are also useful, for example

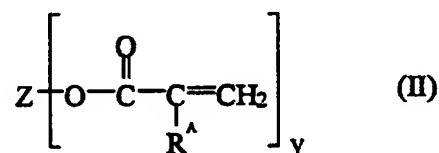


- 10 wherein n is in the range from about 1 to 5, preferably from about 2 to 3, and R³ is an alkyl or aryl moiety that can be halogenated and/or functionalized, and is preferably a perfluoroalkyl group. X is preferably either -C(O)- or -(SO₂)- as previously defined.

The uncured hard coat admixture of the present invention comprises a radiation-curable component; that is, a component that cures upon exposure to radiation (e.g.,
 15 ultraviolet radiation, electron beam radiation, etc.). Preferably, the radiation-curable component is UV-curable.

Useful radiation-curable components must be capable of being combined with the other components of the present invention to provide an uncured antistatic hard coat admixture that provides good wetting and flow characteristics, that allows for a relatively fast cure, and that has a viscosity sufficiently low to be spin coated. For example, the viscosity of an admixture comprising a fluorinated ionic salt, a radiation-curable component, a nonionic perfluoro surfactant, and a radiation-curable silicone-containing compound is preferably no higher than about 100 centipoise at a temperature of 25 C. If the viscosity of the admixture is too high, the admixture may be unsuitable for use with the spin coating techniques which are most desirably used to apply the uncured antistatic hard coat composition to an optical recording media substrate prior to curing. These uncured radiation-curable materials must also, upon being cured, provide abrasion resistance and good adhesion to both polycarbonate and aluminum surfaces.

The radiation-curable component of the present invention can be comprised of one or more monomeric and/or oligomeric radiation-curable components. Each monomeric or oligomeric component may comprise one or more reactive vinyl unsaturated moiety that will polymerize upon being exposed to suitable radiation. Generally, radiation-curable components suitable for the practice of the present invention include (meth)acrylate functional monomers and oligomers having the general formula



wherein R^A is preferably hydrogen or CH_3 , and y is preferably in the range from about 1 to 6. The precise nature of Z is not critical, however Z has a valency y . Representative Z groups include those that comprise, for example, urethanes, polyurethanes, esters, polyesters, oxyalkylene groups, epoxies, alkyl groups, aryl-containing groups, and allyl-containing groups, etc., any of which can be straight, branched, cyclic, aromatic, saturated, or unsaturated.

Preferably, the radiation-curable component of the present invention comprises a (meth)acrylate-functional diluent, a multi-functional (meth)acrylate monomer comprising three or more (meth)acrylate groups, and a multi-functional (meth)acrylate oligomer.

For the purposes of the present invention, (meth)acrylate-functional diluents, also referred to herein as "reactive diluents," are relatively low molecular weight mono- or di-functional, non-aromatic, (meth)acrylate monomers; i.e., y in formula II equals 1 or 2. These relatively low molecular weight reactive diluents are advantageously of a relatively low viscosity, e.g., less than about 30 centipoise (cps) at 25C. Di-functional, non-aromatic (meth)acrylates are generally preferred over mono-functional non-aromatic (meth)acrylates because di-functional non-aromatic (meth)acrylates allow for quicker cure time. Preferred reactive diluents include 1,6-hexanediol di(meth)acrylate (HDODA from UCB Radcure, Inc. of Smyrna, Georgia), tripropylene glycol di(meth)acrylate, isobornyl (meth)acrylate (IBOA, Radcure), 2(2-ethoxyethoxy) ethyl (meth)acrylate (sold under the trade name Sartomer 256 from SARTOMER Company, Inc. of Exton, Pennsylvania), n-vinyl formamide (Sartomer 497), tetrahydrofurfuryl (meth)acrylate (Sartomer 285), polyethylene glycol di(meth)acrylate (Sartomer 344), tripropylene glycol di(meth)acrylate (Radcure), neopentyl glycol dialkoxy di(meth)acrylate, polyethyleneglycol di(meth)acrylate, and mixtures thereof.

Another radiation-curable component useful in the practice of the present invention is the class of multifunctional (meth)acrylate monomers comprising three or more (meth)acrylate groups; i.e., where y in formula II is 3 or greater. Multifunctional (meth)acrylate monomers are useful in the practice of the present invention because they add abrasion resistance to the hard coat layer. Preferred multifunctional (meth)acrylate monomers comprising three or more (meth)acrylate groups include trimethylol propane tri(meth)acrylate (TMPTA), pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, ditrimethylolpropane tri(meth)acrylate (Sartomer 355), dipentaerythritol penta(meth)acrylate (Sartomer 399), dipentaerythritol hydroxy penta(meth)acrylate (DPHPA), glyceryl propoxy tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, and mixtures thereof.

Another useful radiation-curable component of the present invention is the class of multifunctional (meth)acrylate oligomers, having two or more (meth)acrylate groups, and having an average molecular weight (Mw) in the range from about 400 to 2000. Preferred multi-functional (meth)acrylate oligomers include polyester (meth)acrylates, polyurethane (meth)acrylates, and (meth)acrylated epoxy (meth)acrylates. (Meth)acrylated epoxy (meth)acrylates and polyester(meth)acrylates are most preferred because they tend to have a relatively low viscosity and therefore allow a

more uniform layer to be applied by the spin coating method. Specifically, preferred multifunctional (meth)acrylate oligomers include those commercially available from UCB Radcure, Inc. of Smyrna, Georgia and sold under the trade name Ebecryl (Eb): Eb40 (tetrafunctional acrylated polyester oligomer), Eb80 (polyester tetra-functional (meth)acrylate oligomer), Eb81 (multifunctional (meth)acrylated polyester oligomer), Eb600 (bisphenol A epoxy di(meth)acrylate), Eb605 (bisphenol A epoxy di(meth)acrylate diluted with 25% tripropylene glycol di(meth)acrylate), Eb639 (novolac polyester oligomer), Eb2047 (trifunctional acrylated polyester oligomer), Eb3500 (difunctional Bisphenol-A oligomer acrylate), Eb3604 (multi-functional polyester oligomer acrylate), Eb6602 (trifunctional aromatic urethane acrylate oligomer), Eb8301 (hexafunctional aliphatic urethane acrylate), Eb8402 (difunctional aliphatic urethane acrylate oligomer), and mixtures thereof. Of these, the most preferred are, Eb 600, Eb605, Eb80, and Eb81.

Most preferably the radiation-curable component of the present invention comprises multiple radiation-curable components. (Meth)acrylate-functional diluents are preferably present in the radiation-curable component in amounts ranging from about 20 to 60 parts by weight (pbw), based on 100 pbw of radiation-curable material. Multifunctional (meth)acrylate monomers are preferably present in amounts ranging from about 25 to 55 pbw, based on 100 pbw of total radiation-curable component. And, multifunctional (meth)acrylate oligomers, preferably having a molecular weight in the range from 400 to 2000 are preferably present in the radiation-curable component of the present invention in an amount in the range from about 10 to 30 parts by weight, based on 100 parts of radiation-curable component.

Nonionic surfactants useful in the practice of the present invention can be any monomer, oligomer, polymer, or copolymer will facilitate uniform coating of the hard coat composition. Preferably the nonionic surfactant comprises a fluorinated group, and most preferably the nonionic surfactant comprises a perfluorinated group.

One class of preferred nonionic fluorinated surfactants are those that comprise a polyoxyalkylene segment. Of these; especially preferred are those that comprise polyoxyethylene segments. As is explained above, nonionic fluorinated surfactants which comprise a polyoxyethylene segment are believed to be effective within antistatic hard coat compositions because the polyoxyethylene segments of these compounds are believed to form complexes with preferred fluorinated ionic salts. The fluorinated

segment of the nonionic fluorinated surfactant migrates to and orients itself at the coating surface or air interface, bringing to the surface the ionic portion of the fluorinated ionic salt with which it has formed a complex. The fluorinated ionic salt, by being concentrated at the surface of the antistatic hard coat layer, acts very effectively as an antistatic agent to dissipate electrostatic charge.

Nonionic perfluoro surfactants comprising a polyoxyalkylene segment, e.g., polyoxymethylene, polyoxyethylene, polyoxypropylene, etc., preferred in the practice of the present invention, can be represented by one or both of the following general formulas:

10



wherein each y is independently in the range from 1 to 20, preferably 1-8, and most preferably 2; each x represents an average degree of polymerization and independently in the range from 1 to 50, preferably from 10 to 20; and R^5 can be a branched, cyclic, straight, saturated or unsaturated fluorinated carbon chain, including perfluoroalkyl groups, perfluoroalkylene groups, and the like. An occasional carbon-bonded hydrogen atom, bromine atom, or chlorine atom may be present in R^5 ; where present, however, these atoms preferably are present not more than once for every two carbon atoms. Preferably R^5 is $F_{2n+1}C_n^-$ or $F_{2n-1}C_n^-$, and the average n is in the range from 1 to 20. R^6 in formulas III(a-b) is hydrogen, a straight, branched, cyclic, saturated or unsaturated alkyl group, a straight, branched, cyclic, saturated or unsaturated oxy-alkyl group, a (meth)acrylate group, or other similar organic molecules, including any of those defined as R^5 . For example, R^6 may be selected from organic groups such as alkyl groups, phenyl groups, naphthyl groups, alkylphenyl groups, alkylamino groups, alkenylamino groups, alkylthio groups, perfluoroalkenyl or perfluoroalkyl groups, etc. Preferably R^6 is hydrogen or an alkyl group containing from 1 to 10 carbon atoms. It is also possible in formulas III(a-b) for some of the hydrogens in the repeating polyoxyalkylene to be replaced by an alkyl group such as $-CH_3$.

Where R^5 is the perfluorinated group $F_{2n+1}C_n^-$, the nonionic perfluoro surfactant according to formula III.a has the formula



wherein R^6 is preferably hydrogen or an alkyl group, n is preferably in the range from 1 to 12, y is preferably 2, and x is preferably in the range from 1 to 50. Most preferably, R^6 is hydrogen, x average equals 10, y is 2, and n equals 8; formula III.a.1 then becomes



which is commercially available from DuPont, under the trade name ZONYL FSN.

Where R^5 is a perfluoroalkylene group $F_{2n-1}C_n-$, and R^6 is $-CH_3$, nonionic perfluoro surfactants according to formula III.b include those having the general formula



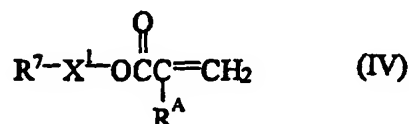
where n is preferably from 3-18, most preferably 9; x is from 1 to 50, preferably from about 10-20, and y preferably is 1 or 2. Where R^5 is a branched perfluorinated alkenyl group R^b , this surfactant becomes:



where R^b is preferably derived from mono-unsaturated tetrafluoroethylene or hexafluoropropylene oligomers, and is most preferably a branched $F_{17}C_9$ group derived from hexafluoropropylene trimer, and x average is about 16, preferably 16.3.

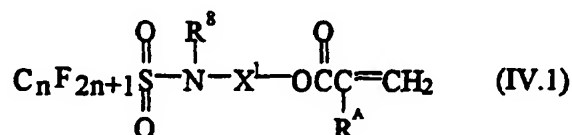
Nonionic perfluoro surfactants comprising polyoxyethylene segments generally can be synthesized by the dehydrofluorinating condensation between a perfluoroalkene and a hydroxy compound having a polyoxyethylene chain. The reaction may be carried out in the presence of a suitable base, such as potassium carbonate, in a reaction solvent such as acetone, methyl ethyl ketone, etc., at about room temperature to 100 C. A general description of the synthesis of these compounds may be found in U.S. Pat. No. 4,272,615.

Another class of surfactant preferred in the practice of the present invention includes (meth)acrylate monomers comprising a fluorinated group, generally represented by formula IV:



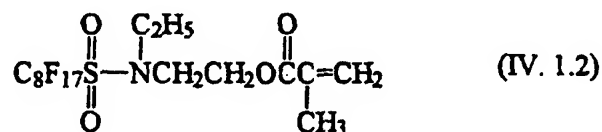
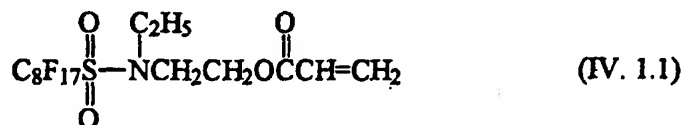
wherein X^1 is a divalent linking group such as an alkyl group, preferably $\text{-CH}_2\text{-}$, or $\text{-CH}_2\text{CH}_2\text{-}$, or a polyether group, preferably $\text{-(OCH}_2\text{CH}_2\text{)}_x\text{-}$ wherein x (average) is preferably in the range from 1 to 20; R^A is preferably hydrogen or CH_3 ; and R^7 is a fluorinated group, preferably, a fluorochemical sulfonamide.

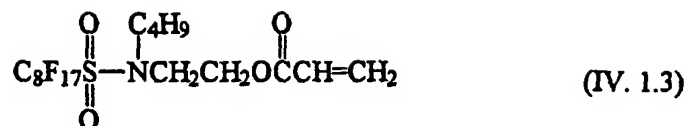
Monomers of formula IV in which R^7 is a fluorochemical sulfonamide may be represented as:



10

wherein n is preferably from about 4 to 12, most preferably 8; R^B is preferably hydrogen or a lower alkyl of from 1-12 carbon atoms such as -CH_3 , $\text{-CH}_2\text{CH}_3$, and the like, most preferably $\text{-CH}_2\text{CH}_3$ or $\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$; X^1 is a divalent linking group such as an alkyl group, preferably $\text{-CH}_2\text{-}$, or $\text{-CH}_2\text{CH}_2\text{-}$, or a polyether group, preferably $\text{-(OCH}_2\text{CH}_2\text{)}_x\text{-}$ wherein x (average) is preferably in the range from 1 to 20; and R^A is preferably hydrogen or a methyl group. Specific monomers according to formula IV.1 include, for example:

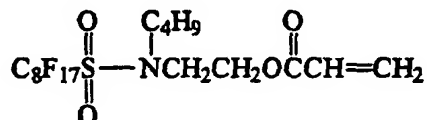




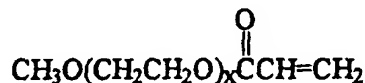
- A further class of preferred nonionic surfactant includes polymers and copolymers comprising pendant perfluorinated groups. A particularly preferred copolymer comprising pendant perfluorinated groups is obtained by copolymerizing about 60-95, preferably 70, parts by weight of a nonfluorinated vinyl monomer having the general formula



- wherein x, y, and z, are preferably chosen to provide an average molecular weight in the range from about 500 to 10000, preferably about 2200; x, y, and z, are preferably in the range from about 7 to 17, 16 to 26, and 7 to 17, respectively, and the ratio of (x+z):y is in the range from about 4:6 to 6:4; with about 5-40, preferably 30, parts by weight of a vinyl monomer comprising a fluorinated group having the formula

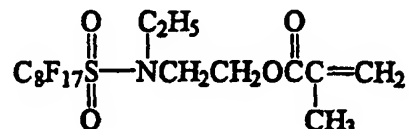


Another particularly preferred copolymer comprising pendant perfluorinated groups can be obtained by copolymerizing about 60-95, preferably 70, parts by weight of a nonfluorinated vinyl monomer having the formula



- wherein x (average) is preferably in the range from about 10 to 25, preferably from about 12 to 18, and is chosen to provide an average molecular weight in the range from

about 500 to 1100, preferably about 600 to 900, with about 5-40, preferably 30 parts by weight of a fluorinated vinyl monomer having the formula

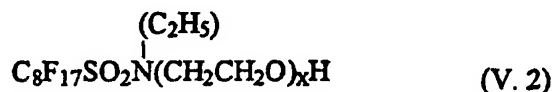
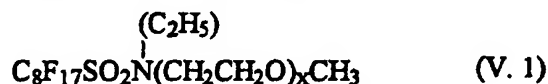


Copolymers comprising pendant fluorinated groups may be prepared by free-radical polymerization methods known in the art. These methods include but are not limited to bulk, solution, emulsion and suspension polymerization methods such as those which have been described in U.S. Pat. No. 3,341,497.

A final class of preferred nonionic surfactant are the nonionic fluorinated surfactants described in U.S. Pat. No. 5,176,943 (Woo) columns 5-6. Of these, the most preferred nonionic fluorinated surfactants are those having the general formula



wherein n is from about 4 to 12; R⁹ is H or a lower alkyl of from 1 to 12 carbon atoms, preferably H or CH₃, R¹⁰ is hydrogen or a lower alkyl of 1-12 carbon atoms, such as H, -CH₃, -CH₂CH₃, etc., and x (average) is from about 1 to 20. Most preferred embodiments of formula V are shown in formulas V.1 and V.2:



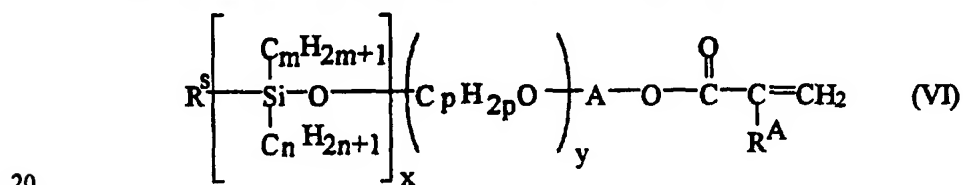
wherein x represents an average degree of polymerization, and is preferably in the range from about 5 to 8, and is most preferably from about 7.2 to 8.

The uncured hard coat composition of the present invention may also optionally comprise a silicone-containing compound. Preferably, the silicone-containing compound may be radiation-curable; i.e., it may comprise one or more vinyl unsaturated moieties that will copolymerize with the radiation-curable component upon being exposed to suitable radiation. By copolymerizing with the radiation-curable component, the radiation-curable silicone-containing compound will become an integral part of the cured hard coat, thus eliminating silicone transfer and silicone contamination problems over

time. Preferably, the vinyl unsaturated group in the radiation-curable silicone-containing compound is a (meth)acrylate group and the radiation-curable silicone-containing compound is a silicone-containing (meth)acrylate compound.

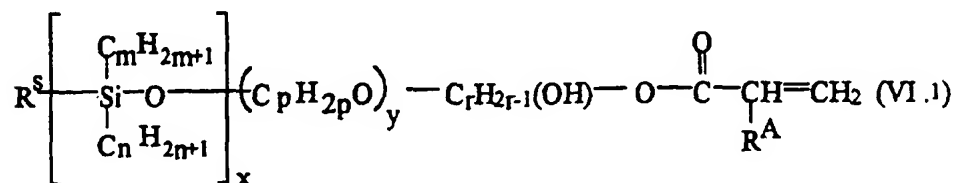
As another advantage, radiation-curable silicone-containing compounds may also
 5 be selected to control their compatibility with the other components of the hard coat composition. For instance, radiation-curable silicone-containing compounds useful in the practice of the present invention preferably comprise a polyoxyalkylene segment (e.g., polyoxymethylene, polyoxyethylene, polyoxypropylene, etc.) that is incorporated into the backbone of the radiation-curable silicone-containing compound. The
 10 polyoxyalkylene segment provides an organic segment which enhances the compatibility of the radiation-curable silicone-containing compound with the acrylic-based radiation-curable component, and allows the radiation-curable silicone-containing compound to be soluble in the radiation-curable component. In the absence of the polyoxyalkylene segment, the radiation-curable silicone-containing compound and the acrylate-based
 15 radiation-curable component may tend to form two phases when combined, leading to haze, orange peel, craters, ghosting, or other surface imperfections upon coating. Preferably, the polyoxyalkylene segment is a polyoxypropylene segment.

One class of preferred radiation-curable silicone-containing compounds are the silicone-containing (meth)acrylate compounds having the general formula

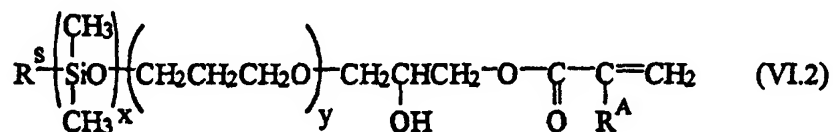


wherein R^A is preferably H or CH_3 , R^s is an alkyl group or hydrogen, A is a hydroxy-containing divalent linking group, x is in the range from 1-9, preferably from 4-7; m, n, and p, are all independently in the range from 1 to 10, preferably m is 1, n is 1, and p is 3.

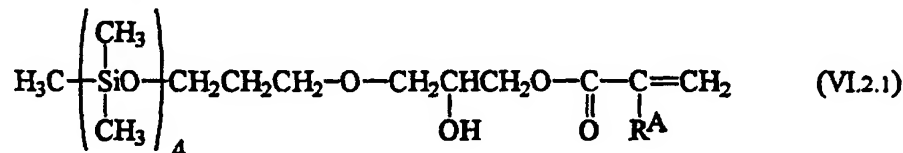
25 Where A is $\text{C}_r\text{H}_{2r-1}$ further comprising a hydroxy group pendant from any of the carbon atoms, formula VI becomes



wherein R^A , R^S , x , y , m , n , and p are defined as above, and r is in the range from 1 to 10, preferably r is 3, and the silicone-containing (meth)acrylate compound is a polydimethylsiloxane. The silicone-containing (meth)acrylate compound is most preferably a polydimethylsiloxane (meth)acrylate having the formula:



wherein R^S and R^A are as defined above, x is in the range from 1-9, preferably from 4-7, and y is in the range from 1-30, preferably from 1-20. Most preferably $x=4$, $y=1$, and R^S is $-\text{CH}_3$ as in the following formula:



wherein R^A is H or CH_3 . This polydimethylsiloxane (meth)acrylate is commercially available from Goldsmith AG, of Essen, Germany under the trade name RC711.

The antistatic hard coat layer of the present invention is a cured composition obtained from an admixture of ingredients comprising various amounts of the fluorinated ionic salt, the nonionic perfluoro surfactant, the radiation-curable component, and the radiation-curable silicone-containing compound. Specifically, we have found that using from about 1 to 4 parts by weight (pbw), preferably from about 1 to 3 pbw, of the fluorinated ionic salt; from about 0.5 to 4 pbw, preferably from about 0.5 to 2 pbw, of the nonionic perfluoro surfactant; from about 95 to 99 pbw, preferably from about 96 to 97 pbw, of the radiation-curable component; and from about 0.5 to 5 pbw, preferably from about 1 to 3 pbw, of the radiation-curable silicone-containing compound, based on 100 pbw of hard coat ingredients, is suitable.

Optionally, the antistatic hard coat compositions of the present invention further comprise a photo initiator which facilitates the curing reaction. Examples of useful photoinitiators include, but are not limited to: Darocure 4265, Irgacure 184, Darocure 1173, and Irgacure 907. These photoinitiators are commercially available from Ceiby Geigy of Hawthorne, New York. The photoinitiator can preferably be present in amounts in the range for 0.25-15 parts by weight, based on 100 parts by weight of radiation-curable material.

Preferably, the antistatic hard coat layers of the present invention are prepared from uncured admixtures of appropriate ingredients which are then applied to optical recording media substrates, such as the magneto optic recording disk 10 of FIG. 1, using a spin coating technique, and then cured by UV (ultraviolet) radiation to form an antistatic hard coat layer.

Admixtures of the uncured hard coat composition of the present invention generally have a viscosity that is sufficiently low to allow spin coating even without any solvent being added to the composition. Spin coating can be accomplished by methods known in the art, and for example, with a Convac coater from Convac of Vaihingen, Germany. Although a solvent is not required for spin coating, a solvent may be advantageous to facilitate the compounding process, i.e., for dissolving raw materials, for extending the shelf life of the finished composition, or for adjusting viscosity of the admixture.

Spin coating allows an extremely uniform coated layer having a thickness of only 0.5 to 20 μm , preferably 0.8 to 10 μm , more preferably 1 to 5 μm , most preferably from 1 to 2 μm , to be easily and quickly formed. To avoid error caused by refraction, it can be desirable that the optical index of the hard coat layer 22 be approximately similar to the optical index of the transparent substrate 14. However, an advantage of providing thin antistatic coatings is that it becomes less important to match these optical indexes, because light passing through a thin coating will experience less refraction.

According to the spin coating technique, an admixture of uncured components of the hard coat layer is prepared. The admixture is delivered onto the substrate 14 of the magneto optic disk 10 using a conventional spin coating apparatus. Such an apparatus generally includes a dispensing needle, a syringe, and a pump. Dispensing the hard coat admixture onto the disk may involve either manually or automatically dispensing the fluid by means of a syringe and a pump. Preferably, the disk to be coated is pre-cleaned with ionized air prior to spin-coating. For admixtures having a viscosity in the range from 5 to 100 centipoise, a needle pressure of 5 to 20 psi (25 to 103 cm Hg) delivers a suitable amount of the admixture onto the center of a disk in about 2 seconds when the disk is spinning at 30 to 50 rpm. Preferably, an in-line filter (0.1 to 2 μm) is used to remove particles from the admixture before the admixture is

allowed to pass through the dispensing needle. After delivery, a high spinoff speed of 1800 to 3500 rpm for 3 to 5 seconds disperses the solution into a thin, uniform coating.

The wet coating is then cured with a suitable form of radiation. Preferably, curing occurs in a chamber fitted with an exhaust fan. Typically, the exhaust fan is
5 operated during curing in order to remove low boiling, volatile components from the oven.

The uncured antistatic hard coat composition of the present invention may be cured using any suitable form of radiation such as electron beam radiation or ultraviolet radiation. It is preferred that the composition be photocurable, i.e., curable with
10 ultraviolet radiation. Various sources of UV radiation are suitable, including electric powered arc lamps, such as medium pressure or high pressure mercury lamps; and electrodeless lamps; such as H-type, D-type, or V-type metal halide lamps. The specific radiation source should be selected to correspond with the absorption spectra of any photoinitiator. As an example, a UV radiation source operating at wavelengths of
15 between 240 to 450 nm and an energy of 200 to 450 mJ/cm² for 4 to 6 seconds would be preferable in the practice of the present invention.

Preferably, spin coating and/or curing occurs in an inert atmosphere. For example, an atmosphere comprising 90% or more nitrogen may be used.

The objects and advantages of the present invention are further illustrated by
20 the following examples, but the particular materials and amounts thereof recited in these examples, as well as the conditions and details, should not be construed to unduly limit this invention.

EXAMPLE 1

This example describes antistatic hard coat sample formulations 1-7, which comprise: UV curable components; the nonionic perfluoro surfactant having the formula:



(designated surfactant A); and fluorinated ionic salts, specifically, lithium tris-(trifluoromethylsulfonyl) methide (designated Salt A), lithium bis-(trifluoromethylsulfonyl)imide (HQ-115) and lithium trifluoromethanesulfonate (FC-122). Table 1 identifies the quantities of the different ingredients for each sample in parts by weight. The mixing of all ingredients in all examples was done at room temperature with a shaker table from Eberbach Corp. of Ann Arbor Michigan.

To produce samples 1 through 7, each fluorinated ionic salt was first dissolved in either a solvent or a (meth)acrylate functional (reactive) diluent. For samples 1 and 2 the reactive diluent SR 285 was charged into a first mixing container. The fluorinated ionic salt was added directly to the reactive diluent and the admixture was shaken for 30 minutes until a homogeneous solution was obtained.

For samples 3-7 the fluorinated ionic salt was first dissolved in isopropanol (IPA) by shaking until a homogenous solution was obtained (20-30 minutes). SR 285 reactive diluent was then added to this solution, which was then shaken for another 30 minutes.

Control 1 was made identically to samples 3-7 except that it did not contain a fluorinated ionic salt.

For all samples, the nonionic perfluorinated surfactant, Surfactant A, was added to the above fluorinated ionic salt solution. The mixture was shaken until the nonionic perfluorinated surfactant had completely dissolved (20-30 minutes).

In a second container, the multifunctional monomers and multifunctional oligomers were mixed. The most viscous component was added first followed by the less viscous components, shaking the mixture between each addition. Reactive diluent HDODA was then added to all samples. The mixture was shaken until the components no longer were visibly separate, followed by 30 minutes of additional shaking.

The admixtures containing the SR(Sartomer) 285, the fluorinated ionic salt, and the nonionic perfluoro surfactant, (and for samples 3-7 and Control 1, IPA), were placed into a syringe and filtered through a 0.20 micron "Acrodisc" filter. The filtrate

was added to the admixture containing the multifunctional monomers and oligomers and HDODA and mixed for 15 minutes.

For samples 1 and 2, the Irgacure 184 photoinitiator was added directly to the above admixture and the resulting admixture was shaken for 30 minutes.

5 For samples 3-7 and Control 1, in a separate container the Irgacure 184 photoinitiator was completely dissolved in IPA by shaking for 15-20 minutes. This solution was placed into a syringe and filtered through a 0.20 micron Acrodisc filter. The filtrate was added to the mixture of fluorinated ionic salt, reactive diluents, IPA, nonionic surfactant, multifunctional monomers, and multifunctional oligomers, and the
10 resulting solution was shaken on the shaker table for another 30 minutes.

The viscosities of uncured hard coat samples 1, 4-7 and Control 1 were measured (in centipoise, cps) with a Brookfield cone and plate viscometer at 10 rpm (revolutions per minute) and 26-27C, with a cone number 42, Model RVDV-II+, from Brookfield Engineering Laboratories, Inc., of Stoughton, MA.

15 The viscosities of uncured hard coat samples 2 and 3 were measured with a Brookfield viscometer with a UL adapter Model DV-II. A Brookfield Model EX-200 Constant Temperature Bath was used to maintain the water temperature at 25C +/- 2C.

Prior to spin coating, the samples were left for 30 minutes to allow any entrapped air to dissipate from the solution. To spin coat, each admixture of uncured
20 hard coat ingredients was manually dispensed onto a polycarbonate disk surface using a disposable syringe outfitted with a 0.2 micron Teflon Acrodisc filter and a needle. The hard coat compositions were spin coated onto the polycarbonate disk substrates. Each disk was rotated for 2-3 seconds at a speed of 30-50 revolutions per minute (rpm) while the hard coat admixture was applied to the disk, followed by a faster spinning cycle of
25 2200 to 3500 rpm for 6-7 seconds.

The applied coatings were subsequently cured to a "tack free" finish by an ultraviolet radiation source in a nitrogen atmosphere. The surfaces of the hard coat layers were examined for cosmetic defects such as streaks, haze, orange peel and oily residue by visual and microscopic inspections. All samples were found to be
30 cosmetically acceptable.

To evaluate the antistatic performance of the cured hard coat layers their surface resistivities were measured at 29-31% relative humidity at 25C using an Electrode Model 803B and recorded with a Galvanometer Model 872 from Electro Tech

Systems, Inc., of Glenside Penn. Residual charge, and 10% decay of 5000 volts, of the cured hard coat layers on clear polycarbonate substrates were measured at 25C and 44-47% humidity using a Model 406D Static Decay Meter from Electro Tech Systems, Inc. The adhesion of the cured hard coat layers to the polycarbonate surfaces was measured
5 according to ASTM D3359-83 (cross hatch adhesion) using a cross-cut tester from BYK-Gardner, Inc., of Silver Springs MD. Pencil hardness was measured according to ASTM D3363-74. Test results are given in Table 1.

TABLE I

Sample:	1	2	3	4	5	6	7	Control 1
Ionic Salt	FC-122 2	FC-122 2	FC-122 2	FC-122 2	FC-122 2	HQ-115 3.63	Salt A 5.2	none
SR 285	10	15	13	13	14	13.78	13.56	14.28
IPA to dissolve fluorinated ionic salt			2	3	3	2.95	2.90	3.06
Surfactant A	1	0.5	1	1	1	1	0.98	1.02
Multifunctional Monomer(s)	SR 344 25 SR-355 15	TMPTA 30	TMPTA 25	TMPTA 30	TMPTA 18 DPHPA 20	TMPTA 17.7 DPHPA 19.66	TMPTA 17.39 DPHPA 19.33	TMPTA 18.37 DPHPA 20.41
Multifunctional Oligomer(s)	Eb 8402 12	Eb 8402 16.5	Eb 8402 10 Eb 81 7.7	Eb 8301 10 Eb 639 5	Eb 81 10	Eb 81 9.85	Eb 81 9.68	Eb 81 10.2
HDXDA	30	30	30	25	22	21.64	21.26	22.45
Irgacure 184	5	6	6	6	6	4	5.8	6.12
IPA to dissolve photoinitiator			4	5	4	3.93	3.87	4.08
Ratio of fluorinated ionic salt to nonionic perfluoro surfactant	2:1	4:1	2:1	2:1	2:1	3.6:1	5.2:1	1:0
Test Results								
Viscosity (cps)	42.6	25.6	20.5	17.0	25.3	25.3	26.6	25.3
Surface Resistivity, Ohms/Square Unit	1.2E+11	1.5E+11	1.4E+11	2.4E+11	1.6E+12	7.0E+11	7.5E+11	>E+13
Residual Charge, Volts	0	0	25	50	-125	25	25	750
10% Decay in sec. to a Residual Charge, of Volts	0.22	0.25	0.33	0.42	5.55	1.36	2.54	>180
Adhesion by Tape	25	50	50	50	50	50	50	5000 (no decay)
Pencil Hardness	5	5	5	5	5	5	5	5
	2H-H	2H-H	2H	2H-H	2H	2H	2H	2H

Table 1 shows the improved antistatic performance of hard coat layers comprising the three different fluorinated ionic salts on the electrical resistivity of the cured hard coats, as compared to Control 1.

Table 2 compares the surface resistivity of samples having the same molar concentration (millimoles per milliliter (mmol/ml)) of the different fluorinated ionic salts. At equal concentrations, HQ-115 and Salt A more effective than FC-122, and HQ-115 is slightly more effective than Salt A.

TABLE 2

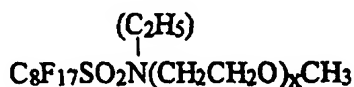
sample	5	6	7
ionic salt	HQ-115	SALT A	FC-122
Concentration of Fluorinated ionic salt (mmol/ml)	0.128M	0.128M	0.128M
Surface Resistivity (Ohms/sq. unit) at 30-31% R.H. 25C	7×10^{11}	7.5×10^{11}	1.6×10^{12}

A higher surface resistivity value indicates a less conductive surface.

EXAMPLE 2

This example describes hard coat samples 8-11, which comprise UV curable components, the fluorinated ionic salts described in Example 1, nonionic perfluorinated surfactants, and a silicone-containing (meth)acrylate compound, specifically, polydimethylsiloxane acrylate. Table 3 describes the amounts of each ingredient for each sample, in parts by weight.

The following procedure was used to produce samples 8-11. The (meth)acrylate functional diluent, HDODA, was placed in a mixing container. The nonionic perfluorinated surfactants defined in Example 1 as Surfactant A, and the nonionic perfluoro surfactant:



wherein x (average) is about 7.2 (designated surfactant B), were added to the HDODA according to Table 3. Next, the fluorinated ionic salts (FC-122, HQ-115, and lithium tris-(trifluoromethylsulfonyl) lithium salt (designated Salt A)) were added according to Table 3. The mixture was shaken by shaker table until the fluorinated ionic salt and nonionic perfluoro surfactant were completely dissolved.

The nonionic perfluorinated surfactant and fluorinated ionic salt must be added to the HDODA prior to the other ingredients, e.g., the multifunctional monomers or

oligomers and the silicone-containing (meth)acrylate. If the fluorinated ionic salt and the nonionic surfactant are added after the other ingredients, the fluorinated ionic salt and nonionic surfactant do not completely dissolve. This leads to a cloudy or two-phase admixture which when coated, results in haze and orange peel and consequently a nonfunctional media.

The remaining ingredients were added to the above admixtures in the following order: multi-functional acrylate monomer trimethylol propane triacrylate (TMPTA); multi-functional oligomers Eb 80, Eb 81, and Eb 605; polydimethylsiloxane acrylate RC 711; and photo initiators Irgacure 184 and Darocure 1173. Small amounts of solvent (methanol or a 50/50 methanol/ethyl acetate mixture) were added to samples 8, 9, and 11 as a means of keeping the ionic-nonionic complexes in solution for a long period of time. The mixture was agitated by shaker table until it formed a homogeneous solution. Viscosities of the hard coat compositions were measured as with samples 2 and 3 of Example 1.

The solutions were coated onto a polycarbonate disk substrate using a Convac laboratory coater. The coatings were dispensed via a luer-lock syringe fitted with a 0.8 micron disposable filter. Each disk was rotated on a Convac laboratory coater for 2-3 seconds at a speed of 30-50 revolutions per minute (rpm) while the hard coat admixture was applied to the disk, followed by a faster spinning cycle of 2200 to 3500 rpm for 6-7 seconds.

The applied coatings were subsequently cured to a "tack free" finish by an ultraviolet radiation source in an air atmosphere.

Surface properties were measured as in Example 1. Additionally, hard coat layer shrinkage was measured by dividing the difference between the density of the cured film and the density of the uncured solution by the density of the uncured solution. Low shrinkage is desirable because it assures that the mechanical properties of the coated media, such as tilt, are not be affected by the hard coat layer.

TABLE 3

	Sample 8	Sample 9	Sample 10	Sample 11	Control 2
HDODA	28	27	25	24.5	26
TMPTA	21	22	30	45.5	46
Eb 605	18	19	20	9	17
Eb 80	7				
Eb 81		7			
Surfactant A			7		
Surfactant B				0.9	1
Zonyl FSN	1	1			
RC 711	2	2	1	1	
Salt A			7.0		
HQ-115				0.9	
FC-122	3.0	2.0			
Irgacure 184	5	5	5	4.5	5
Darocure 1173	5	5	5	4.5	5
Methanol	10	10	0		
Ethyl Acetate/Methanol				4.6/4.6	
Viscosity (cps)	21	18	50	15	42
Test Results					
Surface Resistivity (conditions)	1.5E+12 (77F/56% R.H.)	1.8E+12 (77F/56% R.H.)	>1E+13 (77F/30% R.H.)	5.3E+12 (77F/49% R.H.)	>1E+13 (77F/56% R.H.)
%Shrinkage	10	10	9	11	10
Pencil Hardness	2H	2H	2H-3H	2H	2H

The environmental stability characteristics of the hard coat formulations comprising FC-122/Zonyl FSN and the HQ-115/FC 171 combinations were evaluated using three different accelerated conditions, 80C/85% humidity, 90C/95% humidity, and 100C/100% humidity. The environmental stability of the coatings was evaluated based on the performance of the coatings after each accelerated aging condition. A cured hard coat layer is considered to be environmentally stable if it remains visually perfect after exposure to the accelerated aging conditions; i.e., it does not become hazy, cloudy, delaminated, or show signs of bubbles, or cracking. Table 4 summarized the results.

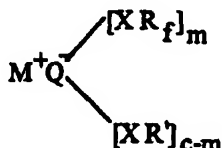
TABLE 4

	80C/85% R.H. for 500 hrs	90C/95% R.H. for 144 hrs	100C/100% R.H. for 120 hrs
Samples 8, 9 FC 122/Zonyl FSN	Surfaces are cloudy, delaminated, and cracking	Surfaces are cloudy, delaminated, and cracking	Surfaces are cloudy, delaminated, cracking and micro-bubbles
Sample 11 HQ-115 / Surfactant B	visually perfect	visually perfect	visually perfect

Table 4 shows that sample 11, which contains HQ-115 and Surfactant B, is stable in conditions of high temperature and high humidity.

What is claimed is:

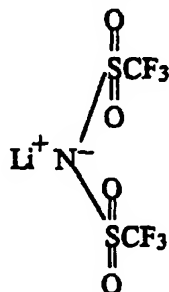
1. An optical recording disk having an antistatic hard coat layer provided on at least one surface of the disk, wherein the antistatic hard coat layer comprises a fluorinated ionic salt of the general formula:



- wherein M^+ represents a cation, Q represents either a carbon atom or a nitrogen atom, each X independently represents a divalent linking group, R_f represents a fluorinated group; and R' represents a monovalent organic group; and
- when Q is carbon, c is 3 and m is 1, 2, or 3; and
- when Q is nitrogen, c is 2 and m is 1 or 2.

2. The optical recording disk of claim 1, wherein Q is carbon.
3. The optical recording disk of claim 1, wherein Q is nitrogen.
4. The optical recording disk of claim 1, wherein R' is an alkyl or aryl group, or a halogen-substituted alkyl or aryl group.
5. The optical recording disk of claim 1, wherein M^+ is Li^+ .
6. The optical recording disk of claim 1, wherein R_f is $\text{C}_n\text{F}_{2n+1}$, where n is in the range from about 1 to 12.
7. The optical recording disk of claim 1, wherein the fluorinated ionic salt is a bis-(perfluoroalkylsulfonyl) imide salt.
8. The optical recording disk of claim 7, wherein the fluorinated ionic salt is a lithium bis-(perfluoroalkylsulfonyl) imide.

9. The optical recording disk of claim 8, wherein the fluorinated ionic salt is lithium bis-(trifluoromethylsulfonyl)imide:

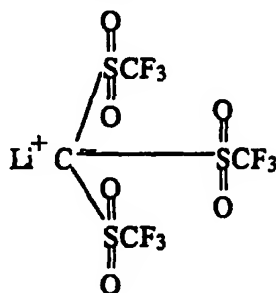


5

10. The optical recording disk of claim 1, wherein the fluorinated ionic salt is a tris-(perfluoroalkylsulfonyl) methide salt.

11. The optical recording disk of claim 10, wherein the fluorinated ionic salt is a lithium tris-(perfluoroalkylsulfonyl) methide.

12. The optical recording disk of claim 11, wherein the ionic salt is lithium tris-(trifluoromethylsulfonyl) methide:



13. The optical recording disk of claim 1, wherein the hard coat layer further comprises a nonionic fluorinated surfactant.

14. The optical recording disk of claim 13, wherein the nonionic fluorinated surfactant comprises a polyoxyethylene segment.

20

15. The optical recording disk of claim 14, wherein the nonionic fluorinated surfactant comprises a perfluorinated group.

16. The optical recording disk of claim 14, wherein the nonionic perfluoro
5 surfactant has the formula:



wherein R^6 is hydrogen or an alkyl group, n is in the range from 1 to 12, and x is in the range from 1 to 50.

10 17. The optical recording disk of claim 15, wherein the nonionic perfluoro surfactant is



18. The optical recording disk of claim 15, wherein the nonionic perfluoro
15 surfactant has the formula:



where x is in the range from 10-20, and n is in the range from 3 to 18.

19. The optical recording disk of claim 18, wherein the nonionic perfluoro
20 surfactant is



20. An optical recording disk having an antistatic hard coat layer provided on at least one surface of the disk, wherein the antistatic hard coat layer is a cured
25 composition obtained from ingredients comprising

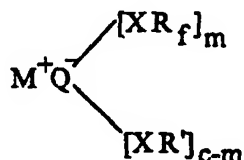
- a) a fluorinated ionic salt;
- b) a radiation-curable component;
- c) a nonionic perfluoro surfactant; and
- d) a radiation-curable silicone-containing compound.

30

21. The optical recording disk according to claim 20, wherein the cured hard coat composition is obtained from

- a) 1-4 parts by weight of a fluorinated ionic salt;
- b) 95-99 parts by weight of a radiation-curable component;
- 5 c) 0.5-4 parts by weight of a nonionic perfluoro surfactant; and
- d) 0.5-5 parts by weight of a radiation-curable silicone-containing compound.

22. The optical recording disk of claim 20, wherein the fluorinated ionic salt has
10 the general formula:



wherein M^+ represents a cation, Q^- represents a carbon atom, a nitrogen atom, or an oxygen atom; each X independently represents a divalent linking group, R_f represents a fluorinated group; and R' represents a monovalent organic group; and

- 15 when Q^- is carbon, c is 3 and m is 1 or 2 or 3;
- when Q^- is nitrogen, c is 2 and m is from 1 or 2; and
- when Q^- is oxygen, c is 1 and m is 1.

23. The optical recording disk of claim 22, wherein Q is carbon.

20

24. The optical recording disk of claim 22, wherein Q is nitrogen.

25. The optical recording disk of claim 22, wherein Q is oxygen.

25 26. The optical recording disk of claim 22, wherein R' is an alkyl or aryl group, or a halogen-substituted alkyl or aryl group.

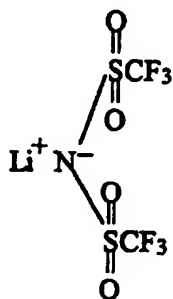
27. The optical recording disk of claim 22, wherein R_f is $\text{C}_n\text{F}_{2n+1}$, and wherein
when Q^- is carbon or nitrogen, n is in the range from 1 to 12, and
30 when Q^- is oxygen, n is in the range from 1 to 3.

28. The optical recording disk of claim 22, wherein M^+ is Li^+ .

29. The optical recording disk of claim 22, wherein the fluorinated ionic salt is a
5 bis-(perfluoroalkylsulfonyl) imide salt.

30. The optical recording disk of claim 29, wherein the fluorinated ionic salt is a lithium bis-(perfluoroalkylsulfonyl) imide.

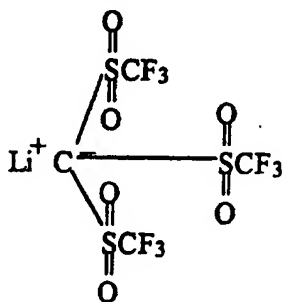
10 31. The optical recording disk of claim 30, wherein the ionic salt is lithium bis-(trifluoromethylsulfonyl)imide:



32. The optical recording disk of claim 22, wherein the fluorinated ionic salt is a
15 tris-(perfluoroalkylsulfonyl) methide salt.

33. The optical recording disk of claim 32, wherein the fluorinated ionic salt is a lithium tris-(perfluoroalkylsulfonyl) methide.

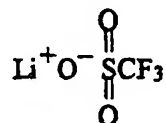
20 34. The optical recording disk of claim 33, wherein the ionic salt is lithium tris-(trifluoromethylsulfonyl) methide:



35. The optical recording disk of claim 22, wherein the fluorinated ionic salt is a perfluoroalkylsulfonate.

5 36. The optical recording disk of claim 35, wherein the fluorinated ionic salt is a lithium perfluoroalkylsulfonate.

37. The optical recording disk of claim 36, wherein the ionic salt is lithium trifluoromethanesulfonate:



10

38. The optical recording disk of claim 20, wherein the nonionic perfluoro surfactant comprises a polyoxyethylene segment.

15 39. The optical recording disk of claim 38, wherein the nonionic perfluoro surfactant is



wherein R^6 is hydrogen or an alkyl group, n is in the range from 1 to 12, and x is in the range from 1 to 50.

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40. The optical recording disk of claim 39, wherein the nonionic perfluoro surfactant is



25 41. The optical recording disk of claim 38, wherein the nonionic perfluoro surfactant has the formula:

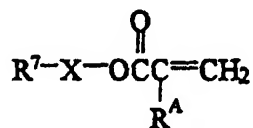


where x is in the range from 10-20, and n is in the range from 3 to 18.

42. The optical recording disk of claim 41, wherein the nonionic perfluoro surfactant has the formula:

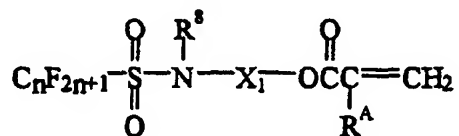


5 43. The optical recording disk of claim 20, wherein the nonionic perfluoro surfactant has the formula



10 wherein R^A is hydrogen or a methyl group, R^7 is a fluorinated group, and X is a divalent linking group.

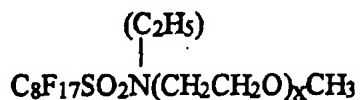
44. The optical recording disk of claim 43, wherein the nonionic perfluoro surfactant has the formula:



15 wherein X_1 is a divalent linking group; R^8 hydrogen or a lower alkyl having from 1-12 carbons; and n is in the range from 4 to 16.

45. The optical recording disk of claim 44, wherein R^8 is an ethyl or butyl group.

20 46. The optical recording disk of claim 20, wherein the nonionic perfluoro surfactant has the formula



25 wherein x is in the range from 1 to 20.

47. The optical recording disk of claim 20, wherein the radiation-curable component comprises

- a) a (meth)acrylate-functional diluent;
- 5 b) a multi-functional (meth)acrylate monomer comprising three or more (meth)acrylate groups; and
- c) a multi-functional (meth)acrylate oligomer.

48. The optical recording disk of claim 47, wherein:

- 10 the (meth)acrylate-functional diluent is a mono- or di-functional non-aromatic (meth)acrylate monomer; and
- the multi-functional (meth)acrylate oligomer has an average molecular weight in the range from 400 to 2000.

15 49. The optical recording disk of claim 48, wherein the radiation-curable component comprises :

- a) 20-60 parts by weight (meth)acrylate-functional diluent;
- b) 25-55 parts by weight multi-functional (meth)acrylate monomer comprising three or more (meth)acrylate groups; and
- 20 c) 10-30 parts by weight multi-functional (meth)acrylate oligomer; based on 100 parts radiation-curable component.

50. The optical recording disk of claim 47, wherein the (meth)acrylate-functional diluent is chosen from the group consisting of: 1,6-hexanediol di(meth)acrylate, tripropylene glycol di(meth)acrylate, bisphenol A epoxy di(meth)acrylate, isobornyl (meth)acrylate, 2(2-ethoxyethoxy) ethyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, polyethylene glycol di(meth)acrylate, n-vinyl formamide, tripropylene glycol di(meth)acrylate, neopentyl glycol dialkoxyl di(meth)acrylate, polyethyleneglycol di(meth)acrylate, and mixtures thereof.

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51. The optical recording disk of claim 50, wherein the (meth)acrylate-functional diluent is 1,6-hexanediol di(meth)acrylate.

52. The optical recording disk of claim 47, wherein the multi-functional (meth)acrylate monomer comprising three or more (meth)acrylate groups is chosen from the group consisting of trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, ditrimethylolpropane tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol hydroxy penta(meth)acrylate, trimethylpropane tri(meth)acrylate, and mixtures thereof.

53. The optical recording disk of claim 52, wherein the multi-functional (meth)acrylate monomer comprising three or more (meth)acrylate groups is chosen from the group consisting of trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, glyceryl propoxy tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, and mixtures thereof.

54. The optical recording disk of claim 47, wherein the multi-functional (meth)acrylate oligomer is chosen from the group consisting of polyester (meth)acrylates, polyurethane (meth)acrylates, and epoxy (meth)acrylates.

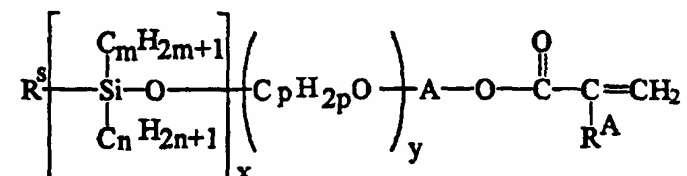
55. The optical recording disk of claim 47, wherein the multi-functional (meth)acrylate oligomer is chosen from the group consisting of: tetrafunctional acrylated polyester oligomer, polyester tetra-functional (meth)acrylate oligomer, multifunctional (meth)acrylated polyester oligomer, bisphenyl A epoxy di(meth)acrylate, trifunctional acrylated polyester oligomer, trifunctional aromatic urethane acrylate oligomer, hexafunctional aliphatic urethane acrylate, difunctional aliphatic urethane acrylate oligomer, and mixtures thereof.

56. The optical recording disk of claim 47, wherein the multi-functional (meth)acrylate oligomer is chosen from the group consisting of: polyester tetra-functional (meth)acrylate oligomer, multifunctional (meth)acrylated polyester oligomer, bisphenol A epoxy di(meth)acrylate, and mixtures thereof.

57. The optical recording disk of claim 20, wherein the radiation-curable silicone-containing compound is a silicone-containing (meth)acrylate compound.

58. The optical recording disk of claim 57, wherein the silicone-containing (meth)acrylate compound comprises a polyoxyalkylene segment.

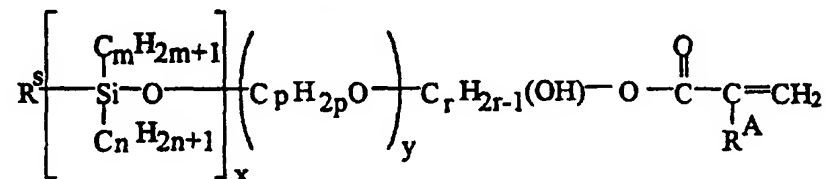
59. The optical recording disk of claim 58, wherein the silicone-containing (meth)acrylate compound has the general formula



wherein R^{A} is hydrogen or a methyl group, R^{S} is hydrogen or an alkyl group, A is a hydroxy-containing divalent linking group, x is in the range from 1-9, y is in the range from 1-30, m, n, and p, are independently in the range from 1 to 10.

10

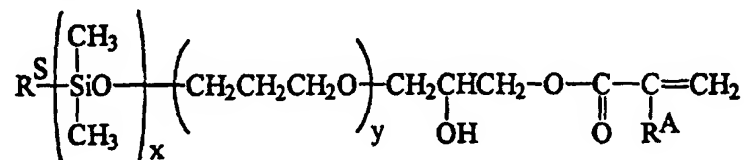
60. The optical recording disk of claim 59, wherein the silicone-containing (meth)acrylate compound has the general formula



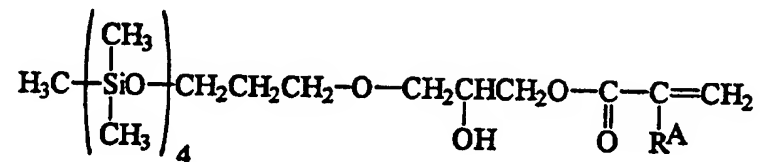
wherein r is in the range of from 1 to 10.

15

61. The optical recording disk of claim 60, wherein the silicone-containing (meth)acrylate compound has the general formula



62. The optical recording disk of claim 61, wherein the silicone-containing compound has the general formula:



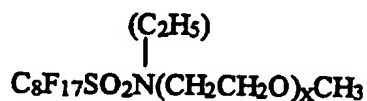
5

63. The optical recording disk of claim 20, wherein:
the fluorinated ionic salt is lithium bis-(trifluoromethylsulfonyl)imide;
the radiation-curable component comprises:

1,6-hexanediol di(meth)acrylate, trimethylpropanetri(meth)acrylate,
bisphenol A epoxydi(meth)acrylate, tripropylene glycol
di(meth)acrylate;

10

the nonionic perfluoro surfactant is:

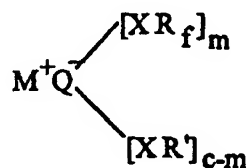


wherein x is in the range from about 5 to 8; and

the silicone-containing (meth)acrylate compound is polydimethylsiloxane
(meth)acrylate.

15

64. A cured antistatic coating composition obtained from ingredients comprising
- a) a fluorinated ionic salt having the general formula:



wherein M^+ represents a cation, Q^- represents a carbon atom, a nitrogen atom, or an oxygen atom; each X independently represents a divalent linking group, R_f represents a fluorinated group; and R' represents a monovalent nonfluorinated group; and

when Q^- is carbon, c is 3 and m is 1 or 2 or 3;

when Q^- is nitrogen, c is 2 and m is from 1 or 2; and

when Q^- is oxygen, c is 1 and m is 1.;

- b) a radiation-curable component;
- c) a nonionic perfluoro surfactant; and
- d) a radiation-curable silicone-containing compound.

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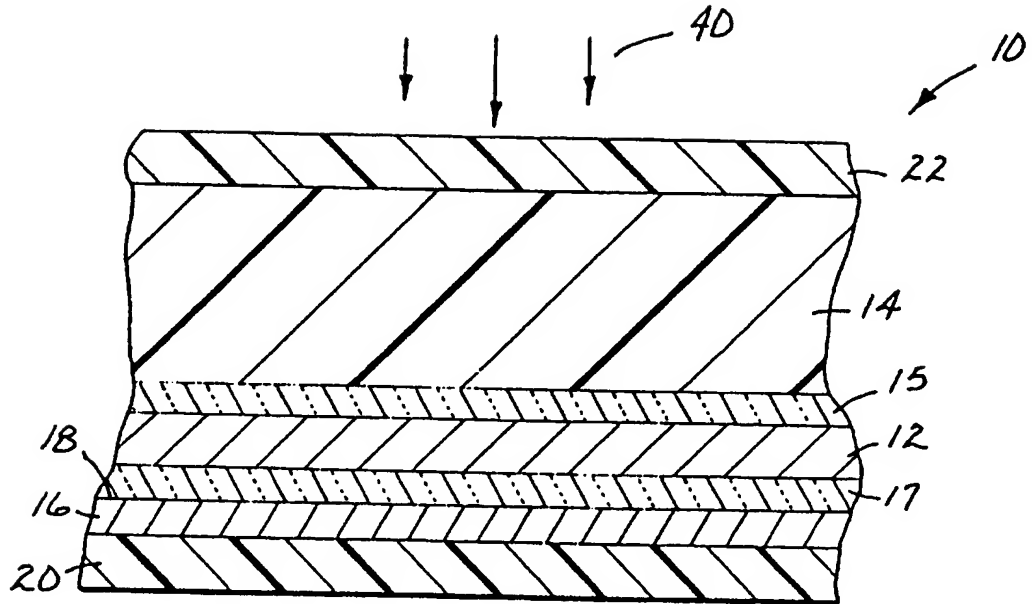


Fig. 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/00442

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G11B7/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,42 22 448 (MINNESOTA MINING AND MANUFACTURING) 14 January 1993 see the whole document ---	1,20
A	WO,A,93 26002 (IMPERIAL CHEMICAL INDUSTRIES) 23 December 1993 see page 5, line 18 - line 23 -----	1,20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search

23 May 1996

Date of mailing of the international search report

- 7. 06. 96

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Heywood, C

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US 96/00442

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-4222448	14-01-93	US-A- 5176943 JP-A- 5214323	05-01-93 24-08-93
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WO-A-9326002	23-12-93	EP-A- 0598096 JP-T- 6509900 US-A- 5475673	25-05-94 02-11-94 12-12-95
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